

Statistical mechanical approach to non equilibrium thermodynamics

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1. Introduction

In the conventional approach to non equilibrium thermodynamics, as presented for instance in Casimir's review article [Casimir, 1945] or in de Groot's monography [de Groot, 1951], based on Onsager's classical work [Onsager, 1931], the following assumptions are believed to be fundamental:

1. Time reversal symmetry (principle of microscopic reversibility)
2. Fluctuation theory
3. The assumption that the phenomenological macroscopic laws of motion (as for example the relation between temperature gradient and flow of heat or between concentration gradient and flow of substance) hold also in the range of fluctuations.

We shall examine these conceptions very briefly.

The principle of microscopic reversibility expresses the invariance of the fundamental microscopic equations of motion of a closed system under time reversal. It holds in quantum mechanics as well as in classical mechanics. The concept of time reversal symmetry was probably first used in statistical mechanics by Loschmidt, who used it in a negative sense as an argument against Boltzmann's H -theorem. Einstein used detailed balance arguments, whose origin is time reversal symmetry, in various connections. Already the early discussions showed that the application of time reversal symmetry to irreversible processes is not completely trivial. A fundamental difficulty is the interpretation of macroscopic measurements on a microscopic level. This problem can be formally—and is usually—neglected as far as classical mechanics can be used for the microscopic description of the system.¹ The reason for this is of course that classical mechanics does not forbid us to assume that an observation can be made arbitrarily detailed and that nevertheless the perturbation of the system caused by the measurement can be made arbitrarily small. This means that the system can be considered as closed in spite of the fact that observations are performed on it. But according to the quantum theory of measurement a system on which observations are made cannot even approximately be considered as closed. On the other hand time reversal symmetry is strictly valid only if the system is

¹ Interesting exceptions are the papers [Green, 1952] and [Yamamoto, 1953]. A forrunner of these is [Zermelo, 1900].

closed. Obviously there is some approximation involved in the application of time reversal symmetry to irreversible processes.

Fluctuation theory is in general used in the form given by Smoluchowski and Einstein [Smoluchowski, 1908], [Einstein, 1910], in which the Boltzmann relation between entropy and probability is reversed and the empirically known dependence of the entropy on observable quantities is used to determine the probability of a deviation from equilibrium in an adiabatically insulated system. In the actual applications Boltzmann's relation is used only to compute the statistical second order moments, the so called covariances of the fluctuating quantities.

It should be remembered that the object of Onsager's original work (in contrast to the more recent papers [Onsager and Machlup, 1953]) was not a theory of the kinetics of fluctuations but the proof of reciprocal relations for the coefficients occurring in the macroscopic equations of flow. The concrete problems considered by Onsager were in fact: Heat conduction in anisotropic crystals, and chemical monomolecular triangle reactions. Fluctuation theory was used only as an, ingenious, artifice for the purpose of obtaining reciprocal relations.

It was particularly stressed by Casimir that Onsager's assumption that macroscopic equations applying originally to deviations large compared with fluctuations, can also be applied to the average behaviour of these fluctuations themselves, is really a new hypothesis. Casimir tried to justify the Onsager assumption qualitatively by associating with the fluctuations a characteristic time interval which is required to establish a state of steady flow. This time interval is assumed to be small compared with the time in which the deviations from equilibrium is appreciably reduced. That means that the macroscopic equations are assumed to be valid for the average behaviour of fluctuations on a "coarse grained" time scale. What Casimir had in mind was apparently an approach to irreversible processes from the kinetic theory of gases by use of the Chapman-Enskog method. Perhaps the most instructive illustration of the necessity of different time scales is however contained already in the beautiful work of Smoluchowski on the connection between diffusion, Brownian motion and coagulation in colloids, [Smoluchowski, 1916].

At present the attempts to establish a direct contact between the kinetics of fluctuations in equilibrium systems and the macroscopic equations of flow in non equilibrium systems are of a rather tentative nature. It therefore seems sound to attack these two problems independently.

Whereas a great number of papers have been concerned with the development of fluctuation theory on the basis of Onsager's hypothesis,¹ the possibility of a direct approach to the macroscopic equations of flow has been almost completely neglected, if we leave out of consideration those works which approach the problem through kinetic theory (Boltzmann's equation) or make use of a master equation and thus replace the original problem by a new, as yet unsolved one, the derivation of the master equation. An exception is the work of Bergmann and Lebowitz [Bergmann and Lebowitz, 1955], [Lebowitz and Bergmann, 1957]. These authors consider a system interacting with a set of infinite heat reservoirs—in the second paper also more general reservoirs are considered. The internal dynamics of the system is assumed to be described completely by its Hamilton function. Its interaction with the reservoirs consists of random im-

¹ In particular [Onsager and Machlup, 1953] and [Hashitsume, 1952, 1956].

pulsive "collisions". Mathematically this is stated in terms of a generalized Liouville equation for the probability density in phase space containing an integral operator (collision term) which takes account of the random interactions with the reservoirs.

The first generalization of Liouville's equation to include the action of a heat reservoir on a system was given by Klein [Klein, 1921, 1922]. In his theory the effect of the random interaction with the surrounding is taken care of by the introduction of a generalized friction and diffusion term into Liouville's equation. Klein's equation may thus also be considered as a generalization of the Smoluchowski-Einstein equation for Brownian motion. Klein's equation generates the transition probability density of a Markov process. The corresponding stationary Markov process is symmetric with respect to time reversal, and may be used as the basis of a kinetic theory of fluctuations.

In Klein's as well as in Bergmann's and Lebowitz' theory the interaction term is constructed so that the probability distribution of the system will in the presence of one reservoir approach a Gibbs' canonical distribution and in the presence of several reservoirs approach a stationary distribution, which is in general not canonical. It can then be demonstrated that Onsager's reciprocal relations are satisfied by the coefficients for heat conduction if the temperature differences between the reservoirs are small. We shall show in this paper that the particular model used by Bergmann and Lebowitz is not necessary for the derivation of Onsager's relations. In fact no special model is needed at all. This is of some importance as the Bergmann Lebowitz formalism is not easily extended to quantum mechanics¹ and also because objections can be raised against the introduction of a phenomenological term into the Liouville equation as this implies a mixing of two different time scales, one fine grained corresponding to the internal dynamics described by the Hamilton function, and one coarse grained corresponding to the interaction with the reservoir.²

2. Outline of some problems connected with Onsager's reciprocal relations

In this section we shall give a survey of some typical fluctuation and transport problems which will be closer examined in later sections from the point of view of general statistical mechanics.

We consider a thermodynamic system which is originally completely closed. Let the macroscopic state of the system be characterized by the values of a set of extensive quantities $A^1, \dots, A^m$

$$A^1 = \alpha^1, \dots, A^m = \alpha^m. \quad (1)$$

Illustrative examples of the extensive quantities A are internal energy and volume of subsystems, number of moles of different species in subsystems etc. The system being closed, the values of the A 's are fixed and show no fluctuation (by definition).

Fluctuations in an open system

Now let the system be brought into contact with a reservoir with which it can exchange the extensive quantities corresponding to A . The reservoir is assumed

¹ See [Willis, 1957].

² Of course such a mixing occurs also in the Boltzmann equation of the kinetic theory of gases.

to be so large compared with the system that its macroscopic state is not affected by this interaction. After some time the system reaches a macroscopic equilibrium state which is characterized by the values of the intensive quantities $B_1, \dots, B_m$

$$B_1 = \beta_1, \dots, B_m = \beta_m \quad (2)$$

which correspond to the extensive quantities A and determine the macroscopic state of the reservoir.

Let the values of the quantities A be measured at different times, after that equilibrium has been reached, and denote by

$$(a^1(t), \dots, a^m(t)) = a(t) \quad (3)$$

the values observed at the time t . In general the values $a(t_1)$ and $a(t_2)$ obtained at different times $t_1 < t_2$, are different and it is natural to call the difference $a(t_2) - a(t_1)$ the flow of A -quantity from the reservoir into the system during the time interval (t_1, t_2) . However when taking a very large number of observations we will find a certain stationary behaviour of the observed values. This is precisely the criterion for equilibrium. Assuming that the values $a(t)$ are produced by some random mechanism we may try to construct models for this mechanism. Ideally such a model should be derived from the microscopic equations of motion, but except for very special cases this has not been possible so far. On the other hand it is usually easy to express invariance properties of the microscopic equations as *symmetries* of the random process associated with the observation series. In particular this is true for time reversal invariance.

Reaction of the system to a sudden change of the constraints

The contact between the system considered above and the reservoir is broken and the system is brought into contact with a second reservoir of the same kind as the first one but in general with different values of the intensive parameters B . Originally the system is not in equilibrium with the second reservoir. As a consequence it will be possible to register average flows of the quantities A from the reservoir into the system. It is quite natural to consider the differences in the intensive parameters B as the "driving forces" producing these average flows. The dependence of the average flows on the differences of intensive parameters is restricted by the time reversal symmetry (valid for the closed system) and for small differences, that is in the domain of a linear approximation Onsager's relations are valid. This will be demonstrated in this paper.

Steady state in contact with several reservoirs

The system considered above is brought into contact with several reservoirs, all of the same kind, but with different values of the intensive parameters B . A steady state, which is in general not an equilibrium state, is assumed to be produced in the system in the course of time. In this steady state the average net flows of the quantities A from all the reservoirs into the system are zero. This means that the different reservoirs are connected by steady flows. The differences of the intensive parameters B may be considered as the "driving forces" of these steady flows. The dependence of the average flows on the differ-

ences is restricted by the time reversal symmetry and in the domain of a linear approximation Onsager's relations are valid. The demonstration is given in this paper.

3. Statistical description of an open system

We shall consider the experimental situation described above as fluctuations in an open system. The intensive parameters B which characterize the state of the reservoir are chosen as the conjugated variables of the extensive variables A with the entropy function, or possibly a generalized entropy function, used as thermodynamic potential. If for instance the A -variables are

$$A: U^{(1)}, \dots, V^{(1)}, \dots, n_1^{(1)}, \dots, n_g^{(1)}, \dots, \quad (4)$$

that is internal energy of subsystem (1), ..., volume of subsystem (1), ..., number of moles of the substance 1 in subsystem (1) ..., the corresponding B -variables are

$$B: \frac{1}{T^{(1)}}, \dots, \frac{p^{(1)}}{T^{(1)}}, \dots, \frac{-\mu_1^{(1)}}{T^{(1)}}, \dots, \frac{-\mu_g^{(1)}}{T^{(1)}}, \dots \quad (5)$$

Here T denotes temperature, p pressure, and μ chemical potential. Upper indices refer to subsystems and lower indices to species of substance. As indicated by the notation we do not necessarily assume that different subsystems are kept at the same temperature, pressure, or chemical potential.

We shall assume that the state of the system at any time is determined by the measurement of an observable $Z = \{Z(1), \dots, Z(n)\}$ whose components $Z(j)$ take values on the real axis. The extensive variables A are assumed to be unique functions of the observable Z

$$a(\zeta) = \{a^1(\zeta), \dots, a^\mu(\zeta), \dots, a^m(\zeta)\}, \quad \zeta = \{\zeta_1, \dots, \zeta_n\}. \quad (6)$$

The observed value of $Z(j)$ as a function of the time may be considered as a realization of a stochastic process $\{z(t, j); -\infty < t < +\infty, j = 1, 2, \dots, n\}$. It is mathematically convenient and physically irrelevant to have the stochastic process defined for all values of the time parameter t on the real axis.

The stochastic process $z(., .)$ associated with the observation of Z is determined by the family of all finite dimensional distribution functions of the form

$$\varrho(t_1, j_1, \dots, t_k, j_k; I_1, \dots, I_k) \quad (7)$$

representing the probability of finding $z(t_1, j_1)$ in the interval I_1 of the real axis, ..., and $z(t_k, j_k)$ in the interval I_k .

If the system has been in contact with the reservoir for a very long time before the measurement of Z starts we are entitled to consider the stochastic process $z(., .)$ corresponding to the observed values of Z as stationary. That is, we assume that

$$\varrho(t_1 + t, j_1, \dots, t_k + t, j_k; I_1, \dots, I_k) = \varrho(t_1, j_1, \dots, t_k, j_k; I_1, \dots, I_k) \quad (8)$$

for every finite dimensional distribution function and every real t . In particular it follows from (8) that the distribution function corresponding to a single instant is independent of the time

$$\varrho(t, 1, 2, \dots, t, n; I_1, \dots, I_n) = \varrho_1(I_1, \dots, I_n), \quad (9)$$

and that the distribution function corresponding to two instants depends on their difference only

$$\varrho(t_1, 1, \dots, t_1, n, t_2, 1, \dots, t_2, n; I_1, \dots, I_{2n}) = \varrho_2(t_2 - t_1; I_1, \dots, I_{2n}). \quad (10)$$

We shall assume that each component of Z has a definite parity under time-reversal (reversal of the direction of the microscopic motion):

$$\theta(j) = +1 \text{ or } -1. \quad (11)$$

If the composite system, including the reservoir, is a closed dynamical system described by classical mechanics or by quantum mechanics and if the stochastic process $z(.,.)$ is stationary one can prove that the stochastic process will also possess the symmetry

$$\varrho(-t_1, j_1, \dots, -t_k, j_k; \theta(j_1)I_1, \dots, \theta(j_k)I_k) = \varrho(t_1, j_1, \dots, t_k, j_k; I_1, \dots, I_k). \quad (12)$$

The result of $\theta(j)$ applied to an interval $I = (a, b)$ is I if $\theta(j) = +1$ and $(-b, -a)$ if $\theta(j) = -1$. For the particular distributions (9) and (10) we obtain in the case of time reversal symmetry

$$\varrho_1(\theta(1)I_1, \dots, \theta(n)I_n) = \varrho_1(I_1, \dots, I_n), \quad (13)$$

showing that the stationary (equilibrium) distribution is invariant under time reversal, and

$$\begin{aligned} \varrho_2(-t, \theta(1)I_1, \dots, \theta(n)I_n, \theta(1)I_{n+1}, \dots, \theta(n)I_{2n}) &= \varrho_2(t, \theta(1)I_{n+1}, \dots, \\ \theta(n)I_{2n}, \theta(1)I_1, \dots, \theta(n)I_n) &= \varrho_2(t, I_1, \dots, I_n, I_{n+1}, \dots, I_{2n}). \end{aligned} \quad (14)$$

The proof of the symmetry relation (12) will not be given in this paper.

The values $\beta_1, \dots, \beta_m$ of the intensive variables B will appear as parameters in every finite dimensional distribution function (7). In particular we shall assume that the stationary distribution $\varrho_1(.,.)$ is of a generalized canonical form [Uhlhorn, 1960 a (7)]

$$\varrho_1(d\zeta_1 \dots d\zeta_n) = \exp \left\{ \frac{1}{\kappa} [Y - \beta_\mu \alpha^\mu(\zeta)] \right\} \mu(d\zeta_1 \dots d\zeta_n) \quad (15)$$

where κ is Boltzmann's constant, and $Y = Y(\beta)$ is the Massieu-Planck function determined by the normalization of (15) and related to the entropy function $S(\alpha)$ by the Legendre transformation

$$S(\alpha) = \alpha^\mu \beta_\mu - Y(\beta), \quad \alpha^\mu = \frac{\partial Y}{\partial \beta_\mu}. \quad (16)$$

The properties of the distribution (15) have been discussed at length in [Uhlhorn, 1960 a], and we shall make the same assumptions about the functions $a^\mu(\zeta)$ as in that paper. The measure $\mu(d\zeta)$ occurring in the definition (15) is independent of the parameters $\beta_1, \dots, \beta_m$. In fact $\mu(d\zeta)$ is determined either by the linear operator in state vector space or by the phase function which is associated with the observable Z , that is $\mu(d\zeta)$ is the structure function of Z .

For the purpose of deriving Onsager's reciprocal relations we do not need the explicit form of any of the distributions (7) except $\varrho_1(\cdot)$. The only properties of the distributions which are needed are the symmetry relations (10) and (12).

4. Hilbert space treatment of the stochastic process

In this section the analytical methods needed for the derivation of Onsager's relation are developed.

Let $\tau = (t, j)$ denote the parameter of the stochastic process $z(\cdot, \cdot)$ associated with the observable Z . We note that $\varrho(\tau_1, \dots, \tau_k; d\zeta_1 \dots d\zeta_k)$ is a probability measure in the k -dimensional Euclidean space R^k . The Hilbert space of all complex functions of k real variables whose square is integrable over R^k with the measure $\varrho(\tau_1, \dots, \tau_k; d\zeta)$ will be called $L^2(\tau_1, \dots, \tau_k)$.

By $H(\tau_1, \dots, \tau_k)$ we shall denote the Hilbert space of all random variables of the form

$$X(z(\tau_1), \dots, z(\tau_k)), X(\zeta_1, \dots, \zeta_k) \in L^2(\tau_1, \dots, \tau_k), \quad (17)$$

with the scalar product

$$\begin{aligned} \langle X_1(z(\tau_1), \dots, z(\tau_k)) | X_2(z(\tau_1), \dots, z(\tau_k)) \rangle &= \\ &= \int_{R^k} \overline{X_1(\zeta_1, \dots, \zeta_k)} X_2(\zeta_1, \dots, \zeta_k) \varrho(\tau_1, \dots, \tau_k; d\zeta_1 \dots d\zeta_k), \end{aligned} \quad (18)$$

and the norm

$$\|X(z(\tau_1), \dots, z(\tau_k))\| = \langle X(z(\tau_1), \dots, z(\tau_k)) | X(z(\tau_1), \dots, z(\tau_k)) \rangle^{\frac{1}{2}}. \quad (19)$$

It is important to observe that though the Hilbert spaces $L^2(\tau_1, \dots, \tau_k)$ and $H(\tau_1, \dots, \tau_k)$ are isometric, according to the definition (18), they are not identical.

The union of all Hilbert spaces $H(\tau_1, \dots, \tau_k)$ determined by a finite number of parameter values of the stochastic process is clearly a linear space with a scalar product corresponding to (18), and after completion a Hilbert space H is obtained. We note that though the elements of a Hilbert space of the type $H(\tau_1, \dots, \tau_k)$ can be analytically characterized with the aid of functions of a finite number of real variables this is no longer the case with the elements of H . The elements of H will nevertheless be called random variables.¹

We can construct a Hilbert subspace of H corresponding to any set $\mathcal{J}$ of parameter values of the stochastic process $z(\cdot, \cdot)$ by forming the union of all Hilbert spaces determined by a finite number of parameter values which belong to the set $\mathcal{J}$. After completion we obtain the Hilbert space $H(\mathcal{J}) \subset H$.

¹ It is not difficult to show that the elements of H are random variables in the usual sense of the word, that is that they can be represented as measurable functions on a probability space.

If x is an arbitrary element in H and $\mathcal{J}$ is a set of parameter values of the stochastic process $z(.,.)$ the orthogonal projection of x into $H(\mathcal{J})$ is called the conditional expectation of the random variable x , given $\{z(\tau); \tau \in \mathcal{J}\}$. For, denoting by $E^{\mathcal{J}}$ the projection on $H(\mathcal{J})$ in H , it is evident that $E^{\mathcal{J}}x$ is the best approximation of x by an element in $H(\mathcal{J})$ if the goodness of the approximation is determined by variance of the random variable $x - E^{\mathcal{J}}x$. That is $E^{\mathcal{J}}x$ is the least square estimate of x . In particular the unconditional expectation of x is equal to its projection onto the Hilbert subspace of constant random variables. This subspace is one-dimensional and is spanned by the unit vector $e \equiv 1$ which evidently is contained in all Hilbert spaces determined by a finite number of parameter values. Hence the expectation of the random variable x can be written

$$Ex = e \langle e | x \rangle. \quad (20)$$

Sets of parameter values of the stochastic process $z(.,.)$ which are determined by conditions on the time variable t only are of particular interest to us. By $H(t)$ we denote the Hilbert subspace of H corresponding to the values $(t, 1) \dots, (t, n)$ of the parameter and by $L^2(t)$ the corresponding function space. Analogously we introduce $H(t_1, \dots, t_k)$ and $L^2(t_1, \dots, t_k)$.

The product of the projections $E^{(\tau_1, \dots, \tau_k)}$ and $E^{(\tau'_1, \dots, \tau'_k)}$

$$E^{(\tau_1, \dots, \tau_k)} E^{(\tau'_1, \dots, \tau'_k)} \quad (21)$$

by the isometry (18) determines a transformation from the function space $L^2(\tau'_1, \dots, \tau'_k)$ into the function space $L^2(\tau_1, \dots, \tau_k)$ which we shall denote by

$$C(\tau_1, \dots, \tau_k; \tau'_1, \dots, \tau'_k). \quad (22)$$

Being isometrically equivalent to the product of two projections the operator (22) is evidently bounded by 1 and in fact its norm is equal to 1 as the unit vector e (20) is transformed into itself by the application of (21). Further the operator (22) has the easily verified property of transforming a non negative function into a non negative function.

So far the discussion applies to any type of stochastic process. We shall now take account of the symmetries (8) and (12), stationarity and invariance under time reversal.

It follows from (8) and the definition of $L^2(t_1, j_1, \dots, t_k, j_k)$ that

$$L^2(t_1 + t, j_1, \dots, t_k + t, j_k) = L^2(t_1, j_1, \dots, t_k, j_k). \quad (23)$$

Hence it is possible to define a transformation $U(t)$ by

$$U(t) X(z(t_1, j_1), \dots, z(t_k, j_k)) = X(z(t_1 + t, j_1), \dots, z(t_k + t, j_k)) \quad (24)$$

where $X(\zeta_1, \dots, \zeta_k)$ is any function belonging to the space (23). The transformation $U(t)$, being bounded in its domain of definition, can be extended to the whole Hilbert space H and gives rise to a one-parameter group of unitary transformations

$$U(t)^* = U(t)^{-1} = U(-t); U(t_1)U(t_2) = U(t_1 + t_2). \quad (25)$$

We shall make the additional assumption that if x is an arbitrary element in H the expression $\langle x | U(t) | x \rangle$ is a continuous function of t .

In order to take account of the time reversal symmetry (12) we define the operator T by

$$TX(z(t_1, j_1), \dots, z(t_k, j_k)) = X(\theta(j_1)z(-t_1, j_1), \dots, \theta(j_k)z(-t_k, j_k)) \quad (26)$$

for any function $X(\zeta_1, \dots, \zeta_k)$ belonging to the space (23). The definition is consistent as it follows from (12) that the function $X(\theta(j_1)\zeta_1, \dots, \theta(j_k)\zeta_k)$ belongs to $L^2(-t_1, j_1, \dots, -t_k, j_k)$. Being evidently bounded on its domain of definition T can be extended to H . It follows from (12) that T is unitary

$$T^* = T^{-1} = T. \quad (27)$$

The involutory property of T is a direct consequence of the definition (26).

From the definitions (24) and (26) we obtain the connection between the group of "kinetic transformations" $U(t)$ and the time reversal operator T

$$TU(t) = U(-t)T. \quad (28)$$

We shall conclude this section by a study of the operator $C(t_1, t_2)$ which is a particular case of the operator (22), defined by (21). The stochastic process $z(\cdot, \cdot)$ being stationary, the function spaces $L^2(t_1)$ and $L^2(t_2)$ are identical both corresponding to the distribution function $\varrho_1(d\zeta)$ defined by (8), and denoting this space by L_1^2 , we find that $C(t_1, t_2)$ is a linear transformation of L_1^2 into itself. From the unitarity of $U(t)$ it follows that

$$U(t)E^{(t)}U(t)^* = E^{(t_1+t)}, \quad (29)$$

and hence the operator $C(t_1; t_2)$ can depend only on the difference $t_2 - t_1$, so that we may write

$$C(t_1; t_2) = C(t_2 - t_1). \quad (30)$$

Recalling the definition of $C(t_1; t_2)$ we find that $C(t)$ has the properties

$$C(0) = 1; C(t)^* = C(-t). \quad (31)$$

The invariance of the stationary distribution $\varrho_1(d\zeta)$ under time reversal (13) makes possible the definition of the operator T in L_1^2

$$TX(\zeta_1, \dots, \zeta_n) = X(\theta(1)\zeta_1, \dots, \theta(n)\zeta_n). \quad (32)$$

The time reversal operator T in L_1^2 is obviously involutory and unitary. It is connected with $C(t)$ by the relation

$$TC(t)T = C(-t), \quad (33)$$

which is easily obtained by applying T (in H) to the projection $E^{(t)}$ and considering the definition of $C(t)$.

The physical meaning of the operator $C(t)$ in L_1^2 is the following. Let the value of the observable Z be observed at the time t_0 and let $X(Z)$ be an arbitrary complex function of the observable Z belonging to the space L_1^2 . We denote the observed value of Z by ζ . The expected value of the observable $X(Z)$ at a time $t_0 + t$ is then given by

$$C(t) X(\zeta). \quad (34)$$

We note that with $X(\zeta)$ and $Y(\zeta)$ in L_1^2 we have identically

$$\begin{aligned} \langle X(z(t_1)) | Y(z(t_2)) \rangle &= \langle X(z(t_1)) | U(t_2 - t_1) | Y(z(t_1)) \rangle = \\ &= \int_{R^n} \overline{X(\zeta)} C(t_2 - t_1) Y(\zeta) \varrho_1(d\zeta). \end{aligned} \quad (35)$$

As we have assumed $U(t)$ to be (weakly) continuous the same holds for $C(t)$. In particular

$$\lim_{t \rightarrow 0} C(t) = 1. \quad (36)$$

There is no restriction from the physical point of view in assuming the stochastic process determined by (7) to be ergodic, or even mixing (compare the discussion given in [Uhlhorn, 1960 b]). Hence the behaviour of $C(t)$ for large values of t is given by

$$\lim_{t \rightarrow +\infty} C(t) X = \int X(\zeta) \varrho_1(d\zeta) = E X, \quad (37)$$

expressing the approach to equilibrium (decay of fluctuations).

5. Fluxes

It was assumed in section 3. that the extensive variables A are unique functions of the observable Z , equation (6). Having associated the observable Z with a stochastic process corresponding to observations of Z when the system is in contact with a specified reservoir we obtain through the functional relation (6) a stochastic process associated with the extensive variables A

$$a(z(t, \cdot)) = \{a^1(z(t, \cdot)), \dots, a^m(z(t, \cdot))\}. \quad (38)$$

The derived stochastic process (38) is obviously stationary with $z(\cdot, \cdot)$ and possesses the time reversal symmetry. In fact the last symmetry relation is satisfied by the process (38) in the strengthened form of *detailed balance*. For it follows from the form of the equilibrium distribution $\varrho_1(d\zeta)$ given by equation (15) that the functions $a^\mu(\zeta)$ must be invariant under the time reversal transformation (32).

The expression

$$\frac{1}{s} [a^\mu(z(t+s, \cdot)) - a^\mu(z(t, \cdot))] (s > 0) \quad (39)$$

is the net flow per unit time of A^μ -quantity from the reservoir into the system during the time interval $(t, t+s)$. The mean value of (39) is zero as a consequence

of the stationarity of the stochastic process. But the conditional mean value of (39) given that

$$z(t, \cdot) = \zeta \quad (40)$$

will in general be different from zero. Using the conditioning operator $C(t)$ defined by (30) we can write the conditional mean value of (39) as

$$\frac{1}{s} [C(s) - 1] a^\mu(\zeta). \quad (41)$$

This does not necessarily require that the function $a^\mu(\cdot)$ belongs to L_1^2 as it may be possible to extend the domain of definition of $C(t)$ beyond this class.

The flux of A^μ -quantity from the reservoir into the system will be defined as the stochastic process $J^\mu(z(t, \cdot))$, where the function $J^\mu(\zeta)$ is defined by

$$J^\mu(\zeta) = \lim_{s \downarrow 0} \frac{1}{s} [C(s) - 1] a^\mu(\zeta). \quad (42)$$

The limit (42) is assumed to exist in the sense that for arbitrary $X(\cdot)$ in L_1^2

$$\lim_{s \downarrow 0} \frac{1}{s} \langle X | C(s) - 1 | a^\mu \rangle = \langle X | J^\mu \rangle. \quad (43)$$

It should be noted that $J^\mu(\cdot)$ depends on the stochastic process $z(\cdot, \cdot)$ through $C(\cdot)$, and hence depends on the particular reservoir. As already mentioned the expectation of $J^\mu(z(t, \cdot))$ is zero

$$E J^\mu(z(t, \cdot)) = 0. \quad (44)$$

Applying the relation (33), which expresses the time reversal symmetry of the operator $C(\cdot)$, to the definition (43) of $J^\mu(\cdot)$ and taking into account that

$$T a^\mu = a^\mu, \quad (45)$$

we find

$$T J^\mu = -J^\mu, \quad (46)$$

that is the fluxes are odd with respect to time reversal as is to be expected.

The discussion given above applies when the system is in contact with any reservoir of the same kind. We shall distinguish between quantities referring to different reservoirs by an index. For instance $J_{(1)}^\mu(\cdot)$ is the flux defined by the stochastic process $z(\cdot, \cdot)_{(1)}$ corresponding to contact with reservoir number (1), with the parameter values $\beta_{1(1)}, \dots, \beta_{m(1)}$.

6. Reaction of the system to a sudden change of the constraints

The physical situation has been described in section 2. The system has been for a long time in contact with reservoir number (1). At a certain time t_0 , (1) is replaced by another reservoir of the same kind (2). The observations of the "state" of the system consist in the measurement of the observable Z (section

3.), which is associated with the stochastic processes $z(\dots)_{(1)}$ and $z(\dots)_{(2)}$, when the system is in contact with reservoirs (1) and (2) respectively. For times prior to t_0 we may use the stochastic process $z(\dots)_{(1)}$ to describe the observed values of Z . The stationary distribution $\varrho_{1(1)}(\dots)$ is the generalized canonical distribution (15) determined by the parameter values $\beta_{1(1)}, \dots, \beta_{m(1)}$. After the instant t_0 the observed values of Z cannot in general be associated with a stationary stochastic process. It is however reasonable to assume that it is possible to describe the situation after t_0 by the conditional process derived from the stationary stochastic process $z(\dots)_{(2)}$. As the last process is assumed to be mixing in the sense of [Hopf, 1937], which in particular implies (37), the system will ultimately reach a new equilibrium state corresponding to a generalized canonical equilibrium distribution $\varrho_{1(2)}(\dots)$ determined by the parameter values $\beta_{1(2)}, \dots, \beta_{m(2)}$.

As a consequence of the non stationary character of the stochastic process associated with the observation of Z , the mean values $\alpha^1, \dots, \alpha^m$ of the stochastic variables $a^1(t), \dots, a^m(t)$, defined by (38), will be time dependent for $t > t_0$. Only if the two sets of parameters $\beta_{(1)}$ and $\beta_{(2)}$ are equal will the mean values be time independent. We can therefore expect a phenomenological relation of the form

$$\alpha^\mu(t_0 + t) - \alpha^\mu(t_0) = L^{\mu\nu}(t) \Delta\beta_\nu \quad (\Delta\beta_\mu = \beta_{\mu(2)} - \beta_{\mu(1)})^1 \quad (47)$$

to be valid to the first order in $\Delta\beta_\mu$.

We shall show that the coefficients

$$L^{\mu\nu}(t) = \left\{ \frac{\partial}{\partial \Delta\beta_\nu} [\alpha^\mu(t_0 + t) - \alpha^\mu(t)] \right\}_{\Delta\beta=0} \quad (48)$$

obey Onsager's reciprocal relations

$$L^{\mu\nu}(t) = L^{\nu\mu}(t). \quad (49)$$

Proof of reciprocal relations

Denote the index of probability corresponding to the equilibrium distributions $\varrho_{1(1)}$ and $\varrho_{1(2)}$ by

$$\sigma_{(r)}(\zeta) = \frac{1}{Z} [Y(\beta_{(r)}) - \beta_{\mu(r)} a^\mu(\zeta)] \quad (r=1,2). \quad (50)$$

According to our assumption, which is justified by the largeness of the reservoir (2) and the smallness of $\Delta\beta_\mu$, we have

$$\alpha^\mu(t_0 + t) - \alpha^\mu(t_0) = \int [C(t)_{(2)} - 1] a^\mu(\zeta) \exp \{ \sigma_{(1)}(\zeta) \} \mu(d\zeta), \quad (51)$$

where $C(t)_{(2)}$ is the conditioning operator of the stochastic process $z(\dots)_{(2)}$. The relation (48) is equivalent to

$$L^{\mu\nu} = \left\{ - \frac{\partial}{\partial \beta_{\nu(1)}} [\alpha^\mu(t_0 + t) - \alpha^\mu(t_0)] \right\}_{\beta_{(1)} = \beta_{(2)}}. \quad (52)$$

¹ Summation convention, $\mu = 1, \dots, m$.

and inserting (51) into this expression we obtain

$$L^{\mu\nu} = \frac{1}{\mathcal{N}} \int [C(t)_{(2)} - 1] a^\mu(\zeta) a^\nu(\zeta) \exp\{\sigma_{(2)}(\zeta)\} \mu(d\zeta), \quad (53)$$

as

$$\beta_{(1)} = \beta_{(2)} \text{ implies } \sigma_{(1)}(\zeta) = \sigma_{(2)}(\zeta). \quad (54)$$

The expression (53) can also be written as a scalar product in $L^2_{1(2)}$

$$L^{\mu\nu} = \frac{1}{\mathcal{N}} \langle a^\nu | C(t)_{(2)} - 1 | a^\mu \rangle_{(2)}, \quad (55)$$

and using the properties (31) and (33) of $C(t)_{(2)}$, recalling (45), we find that (55) is equal to

$$\frac{1}{\mathcal{N}} \langle a^\mu | C(t)_{(2)} - 1 | a^\nu \rangle_{(2)} = L^{\nu\mu}. \quad (56)$$

This is the desired result (49).

7. Steady state in contact with several reservoirs

The physical situation was described in section 2. The system is in simultaneous contact with a number of mutually independent reservoirs ($r=1, 2, \dots$) of the same kind but with slightly different values of the parameters B

$$\beta_{1(r)}, \dots, \beta_{m(r)} \quad (r=1, 2, \dots). \quad (57)$$

It is assumed that macroscopically the system reaches a steady state. This steady state is an equilibrium state only if the parameter sets (57) corresponding to different r are equal.

As above the observation of the system consists in the measurement of the observable Z . The series of observations of Z is associated with a stationary stochastic process, stationarity of the stochastic process corresponding to the fact that macroscopically the system is in a steady state. As however the total system, including the reservoirs, is not in equilibrium we cannot assume that the stationary stochastic process possesses time reversal symmetry. We denote the stationary stochastic process by $z(\cdot, \cdot)_0$, and write

$$\beta_{\mu(r)} = \beta_\mu + \Delta\beta_{\mu(r)} \quad (\mu=1, \dots, m; r=1, 2, \dots). \quad (58)$$

We are interested in the case when the differences $\Delta\beta_{\mu(r)}$ are small. Let the equilibrium distribution of the stochastic process $z(\cdot, \cdot)_0$ be determined by the index of probability $\sigma(\cdot)$ which for vanishing $\Delta\beta_{\mu(r)}$ reduces to the canonical form

$$\sigma_0(\zeta) = \frac{1}{\mathcal{N}} [Y(\beta) - \beta_\mu a^\mu(\zeta)]. \quad (59)$$

Further we introduce the stochastic processes $z(.,.)_{(r)}$ ($r=1, 2, \dots$) which correspond to the observation of Z when the system is in contact with a single reservoir (r). These processes are stationary and possess time reversal symmetry. Their equilibrium distributions are of the generalized canonical form. We introduce the derivative of the conditioning operator

$$M_{(r)} = \lim_{t \downarrow 0} \frac{1}{t} [C(t)_{(r)} - 1]. \quad (60)$$

This limit is assumed to exist in the sense

$$\langle X | M_{(r)} | Y \rangle_{(r)} = \lim_{t \downarrow 0} \frac{1}{t} \langle X | C(t)_{(r)} - 1 | Y \rangle_{(r)} \quad (61)$$

for certain $X(.)$ and $Y(.)$ in $L^2_{1(r)}$. It follows at once from the properties (31) and (33) of $C(t)_{(r)}$ that

$$\langle X | M_{(r)} | Y \rangle_{(r)} = \langle T Y | M_{(r)} | T X \rangle_{(r)} \quad (62)$$

if $X(.)$ and $Y(.)$ are real functions.

The superposition assumption

We shall assume the following connection between the stochastic processes $z(.,.)_0$ and $z(.,.)_{(r)}$ ($r=1, 2, \dots$). In the limit of small differences $\Delta \beta_{\mu(r)}$, for $X(.)$ in the domain of definition of $M_{(r)}$

$$\sum_{r=1}^{\infty} \int M_{(r)} X(\zeta) \exp \{ \sigma(\zeta) \} \mu(d\zeta) = 0 \quad (|\Delta \beta|^2). \quad (63)$$

The condition (63) is to be understood in the sense that

$$\left[\sum_{r=1}^{\infty} \int M_{(r)} X(\zeta) \exp \{ \sigma(\zeta) \} \mu(d\zeta) \right]_{\Delta \beta=0} = 0, \quad (64)$$

$$\text{and} \quad \left\{ \frac{\partial}{\partial \Delta \beta_{\nu(r)}} \sum_{r=1}^{\infty} \int M_{(r)} X(\zeta) \exp \{ \sigma(\zeta) \} \mu(d\zeta) \right\}_{\Delta \beta=0} = 0. \quad (65)$$

The first relation (64) is a direct consequence of the fact that for $\Delta \beta=0$ the index of probability $\sigma(.)$ reduces to the canonical form (59), and the fact that, the stochastic processes $z(.,.)_{(r)}$ being stationary, the mean value of $X(z(t,.)_{(r)})$ is independent of t :

$$\begin{aligned} \frac{\partial}{\partial t} E X(z(t,.)_{(r)}) &= \lim_{t \downarrow 0} \frac{1}{t} \int [C(t)_{(r)} X(\zeta) - X(\zeta)] \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = \\ &= \int M_{(r)} X(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = 0. \end{aligned} \quad (66)$$

The second relation (65) on the other hand represents a new assumption, though a rather weak and natural one. Its precise meaning will become clear below.

The flux of A^μ -quantity from the reservoir (r) into the system has been defined in section 5. as the stochastic variable

$$J_{(r)}^\mu(z(t, \cdot)_0); J_{(r)}^\mu(\zeta) = M_{(r)} a^\mu(\zeta). \quad (67)$$

The mean value of this stochastic variable in the steady state will be denoted

$$J_{(r)}^\mu = E J_{(r)}^\mu(z(t, \cdot)_0) = \int M_{(r)} a^\mu(\zeta) \exp \{ \sigma(\zeta) \} \mu(d\zeta). \quad (68)$$

As a consequence of the superposition assumption (63) we obtain the necessary condition for a steady state

$$\sum_{r=1} J_{(r)}^\mu = 0 (|\Delta\beta|^2), \quad (69)$$

expressing the conservation of A^μ -quantity. It should be observed that it is only in the limit of small differences $\Delta\beta_{\mu(r)}$ possible to define the fluxes from individual reservoirs (67). Hence it is sufficient that (69) holds to the second order in $\Delta\beta_{\mu(r)}$.

In the limit of small $\Delta\beta_{\mu(r)}$ we expect a linear relation of the form

$$J_{(r)}^\mu = \sum_{r'=1} L_{(r)(r')}^\mu \Delta\beta_{\nu(r')} + 0 (|\Delta\beta|^2), \quad (70)$$

between fluxes and affinities. We shall prove that the phenomenological coefficients

$$L_{(r)(r')}^\mu = \left[\frac{\partial}{\partial \beta_{\nu(r')}} J_{(r)}^\mu \right]_{\Delta\beta=0} \quad (71)$$

satisfy Onsagers's reciprocal relations

$$L_{(r)(r')}^\mu = L_{(r')(r)}^\mu. \quad (72)$$

Proof of reciprocal relations

Take $X(\zeta) = 1$ in (62). In view of (66)

$$\int M_{(r)} Y(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = 0. \quad (73)$$

Differentiate (73) with respect to $\beta_{\mu(r)}$:

$$\begin{aligned} \int \left[\frac{\partial}{\partial \beta_{\mu(r)}} M_{(r)} Y(\zeta) \right] \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) - \\ - \frac{1}{\mathcal{N}} \int [M_{(r)} Y(\zeta)] a^\mu(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = 0 \end{aligned} \quad (74)$$

and use the symmetry relation (62), recalling that $\sigma_{(r)}(\zeta)$ and hence $a^\mu(\zeta)$ is T -invariant:

$$\begin{aligned}
 & \int \left[\frac{\partial}{\partial \beta_{\mu(r)}} M_{(r)} Y(\zeta) \right] \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = \\
 & = \frac{1}{\kappa} \int [M_{(r)} Y(\zeta)] a^\mu(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = \\
 & = \frac{1}{\kappa} \int [T Y(\zeta)] [M_{(r)} a^\mu(\zeta)] \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = \\
 & = \frac{1}{\kappa} \int [T Y(\zeta)] J_{(r)}^\mu(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta). \quad (75)
 \end{aligned}$$

Take in particular $Y(\zeta) = a^v(\zeta)$:

$$\begin{aligned}
 & \int \left[\frac{\partial}{\partial \beta_{\mu(r)}} J_{(r)}^v(\zeta) \right] \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = \\
 & = \frac{1}{\kappa} \int J_{(r)}^v(\zeta) a^\mu(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = \\
 & = \frac{1}{\kappa} \int J_{(r)}^\mu(\zeta) a^v(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) = \\
 & = \int \left[\frac{\partial}{\partial \beta_{\nu(r)}} J_{(r)}^\mu(\zeta) \right] \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta). \quad (76)
 \end{aligned}$$

Let

$$\sigma_{(r)\mu}(\zeta) = \left[\frac{\partial}{\partial \Delta \beta_{\mu(r)}} \sigma(\zeta) \right]_{\Delta \beta=0} \quad (77)$$

and consider the superposition assumption (65)

$$\begin{aligned}
 0 &= \left[\frac{\partial}{\partial \Delta \beta_{\mu(r)}} \sum_{r=1} \int M_{(r)} Y(\zeta) \exp \{ \sigma(\zeta) \} \mu(d\zeta) \right]_{\Delta \beta=0} = \\
 &= \left[\int \frac{\partial M_{(r)} Y(\zeta)}{\partial \beta_{\mu(r)}} \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta \beta=0} + \\
 &+ \left[\sum_{r'=1} \int [M_{(r')} Y(\zeta)] \sigma_{(r)\mu}(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta \beta=0}. \quad (78)
 \end{aligned}$$

Combine (78) with (75):

$$\begin{aligned}
 & \frac{1}{\kappa} \left[\int T Y(\zeta) J_{(r)}^\mu(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta \beta=0} = \\
 & = - \left[\sum_{r=1} \int M_{(r)} Y(\zeta) \sigma_{(r)\mu}(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta \beta=0}. \quad (79)
 \end{aligned}$$

Take in particular $Y(\zeta) = T \sigma_{(r')\nu}$ and use the symmetry relation (62)

$$\begin{aligned}
 & \left[\int \sigma_{(r')\nu}(\zeta) J_{(r)}^{\mu}(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta\beta=0} = \\
 & = -\kappa \left[\sum_{r''=1} \int (M_{(r'')} T \sigma_{(r')\nu}(\zeta)) \sigma_{(r)\mu}(\zeta) \exp \{ \sigma_{(r'')}(\zeta) \} \mu(d\zeta) \right]_{\Delta\beta=0} = \\
 & = -\kappa \left[\sum_{r''=1} \int (M_{(r'')} T \sigma_{(r)\mu}(\zeta)) \sigma_{(r')\nu}(\zeta) \exp \{ \sigma_{(r'')}(\zeta) \} \mu(d\zeta) \right]_{\Delta\beta=0} = \\
 & = \left[\int \sigma_{(r)\mu}(\zeta) J_{(r')}^{\nu}(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta\beta=0}.
 \end{aligned} \tag{80}$$

The coefficient $L_{(r)(r')}^{\mu \nu}$ is according to (71)

$$\begin{aligned}
 L_{(r)(r')}^{\mu \nu} &= \delta_{r,r'} \left[\int \frac{\partial J_{(r)}^{\mu}(\zeta)}{\partial \beta_{\nu(r)}} \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta\beta=0} + \\
 &+ \left[\int J_{(r)}^{\mu}(\zeta) \sigma_{(r')\nu}(\zeta) \exp \{ \sigma_{(r)}(\zeta) \} \mu(d\zeta) \right]_{\Delta\beta=0}.
 \end{aligned} \tag{81}$$

The terms to the right are identical with the expressions (76) and (80) which have the desired symmetry, so that finally

$$L_{(r)(r')}^{\mu \nu} = L_{(r')\mu}^{\nu} \tag{82}$$

8. Discussion

It should be observed that the results of this work have been obtained, without any other assumption than the validity of time reversal symmetry for observation series in equilibrium systems. This is a reasonable assumption, as it can be proved for closed systems in macroscopic equilibrium, and is independent of whether quantum or classical mechanics is used for the microscopic description of the system. It is evident that any particular model for the interaction between system and reservoirs, which is in agreement with time reversal invariance, will give the results obtained here. It is easy to see that the models of Klein and of Bergmann and Lebowitz have this property.

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